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**Studies on Corrosion of Aluminum Alloys by JP-10 Fuel
Using Electrochemical Impedance Spectroscopy**

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ABSTRACT

A Government Industry Data Exchange Program alert has been issued that states that the fuel system icing inhibitor (FSII) in JP-10 fuel is corroding aluminum components in missile fuel systems during long-term storage under an anhydrous nitrogen atmosphere. Previous investigations into fuel-system corrosion have used extreme conditions such as high FSII concentration or temperature to accelerate corrosion. To better understand the effects of fuel additives on corrosion of aluminum alloy components, electrochemical impedance spectroscopy (EIS) was used to determine the corrosion rate as a function of additive type and concentration under conditions similar to those found in actual use. This paper presents the EIS results of corrosion studies conducted on Al 2024, Al 6061, Al A357, and Al 7075. The effects of concentration of the FSII, presence and absence of butylated hydroxytoluene, effect of water concentration, effect of temperature, and effects of coating on corrosion rates of these alloys will be presented and discussed in detail.

INTRODUCTION

Corrosion of the aluminum alloy fuel system components has been discovered in missiles fueled with JP-10. Missiles in which corrosion was discovered have been stored for long periods of time in temperature environments ranging from approximately -8 °C to 30 °C. An anhydrous nitrogen pad was placed in the fuel tank and exposed surfaces were coated to inhibit corrosion. The corrosion of the fuel system components was found to be localized pitting corrosion.

The Military Specification JP-10 is a synthetic hi-density fuel, the base component of which is Exo-Tetrahydrodi (cyclopentadiene), also known as C-10. The primary additives are an antioxidant, approximately 100 ppm of butylated hydroxytoluene (BHT), and a fuel system icing inhibitor (FSII). Typically the fuel will contain small traces of water (20-50 ppm). The FSII, as specified, is approximately 0.1 percent of either ethylene glycol monomethyl ether (EGME) or diethylene glycol monomethyl ether (DiEGME). It has been proposed that the FSII additives are responsible for the corrosion of the Al alloys.

Corrosion studies using immersion test methods similar to ASTM [1] have been shown to provide decisive results; however, conventional immersion testing is a lengthy process and is inconvenient for studies involving many variables the interaction of which is unknown. Because of these drawbacks, both DC and AC electrochemical methods have been developed to provide accelerated corrosion results which can be compared with long-term immersion experiments. Of the two electrochemical test methods, AC electrochemical impedance spectroscopy (EIS) is finding increased usage in the investigation of corrosion of bare metals [2-4] and also of coated systems [5-9]. In particular, EIS has been found to be very sensitive in the determination of pitting corrosion of aluminum [10]. One of the difficulties encountered in the application of electrochemical techniques is in the study of low conductivity media such as JP-10 fuel.

EIS has been used to investigate corrosion in nonaqueous low-conductivity media. Lawton et. al. [11], used EIS to study the corrosion of stainless steels AM 350 and AM 355 in nonaqueous media where very small differences in corrosion rates of these alloys in hydrazine were determined. Ontiveros et. al. [12], used EIS to study the corrosion behavior of mild steel coated with low conductivity inorganic zinc-rich primers in aqueous and nonaqueous solutions. Based on this previous research it was felt that EIS could be successfully applied to the investigation of corrosion of aluminum alloys in JP-10.

This paper describes the method used and the results of testing to determine the effect on corrosion current of concentration of FSII, presence and absence of BHT, temperature, and coating for several aluminum alloys.

EXPERIMENTAL

A Schlumberger potentiostat 1286 in conjunction with a 1260 impedance gain phase analyzer were used for the impedance measurements. The data were recorded between 1000 KHz and 1 Hz. An AC amplitude of 100 mV was used to collect data in the frequency range.

The electrochemical glass cell (Figure 1) was 7.04-cm-diameter and 2.05-cm long. The cell had an inlet and outlet for nitrogen purge which was also used for filling the cell with the fuel mixture. An aluminum

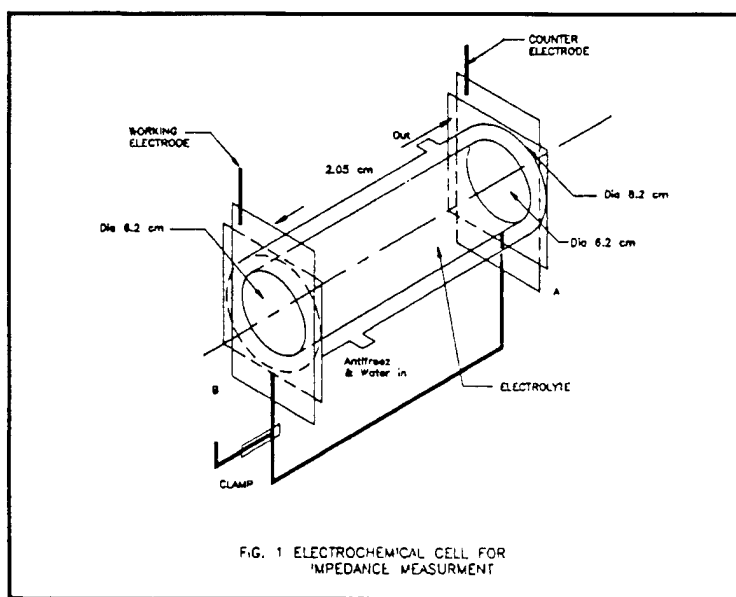


Figure 1
Schematic of Electrochemical Cell

test specimen and a viton gasket were placed on each end of the glass cell. The viton gasket had a 6.4-cm-diameter hole exposing the Al plates to the electrolyte (fuel mixture). The electrochemical cell for lower temperature studies was a double jacketed cylindrical cell. Temperature was maintained by circulating a water/antifreeze mixture from a controlled temperature bath through the outer jacket. The temperature of the electrolyte was monitored by a thermocouple.

The experiments reported here were conducted after purging nitrogen through the electrolyte and a nitrogen atmosphere was maintained in the cell. The aluminum plates served as the working electrode and the counter electrode. The working electrode was attached to the reference lead of the instrument making it the reference electrode.

Alloys tested were Al 2024, Al A357, Al 7075 and Al 6061. The EGME and DiEGME concentration was varied between 0.1 and 100 percent. The concentration of BHT was either 0 or 100 ppm. Water concentration was maintained at 22 ppm for the results reported here. Experiments were conducted at ambient temperature (23 ± 3 °C) except in controlled temperature experiments. The controlled temperature experiments were conducted at 0, 8 and 25 °C. For experiments with uncoated alloys the samples were polished with 600 grit Al_2O_3 powder to a consistent surface finish. Three coating systems were investigated, chromic acid anodization, Scotchweld EC 1290® which is an epoxy polyamide coating, and a chemical conversion coating. The coating systems were tested both individually and in combination (if applicable to the missile system).

RESULTS AND DISCUSSION

Effect Of Fuel Additives

Figure 2 is a plot of the corrosion current for uncoated Al 2024 measured after 22 days of exposure to C-10 with varying concentrations of EGME with and without BHT. The corrosion current is shown to increase over six orders of magnitude as the concentration of EGME increases in the C-10 fuel; however, the magnitude of the increase is less for C-10 solutions with BHT added. The corrosion current in 0.1 percent EGME in the absence of BHT was observed to be $1.955 \times 10^{-2} \mu\text{A}$ which increased to 4814 μA in 100 percent EGME. The change in EGME concentration from 0.1 percent to 100 percent in the presence of BHT

changed the corrosion rate from $1.648 \times 10^{-2} \mu\text{A}$ to $883 \mu\text{A}$. Similar trends were observed for solutions with DiEGME added. These results indicate that the corrosion of Al 2024 increases as a function of FSII concentration and that BHT has an inhibiting effect on corrosion.

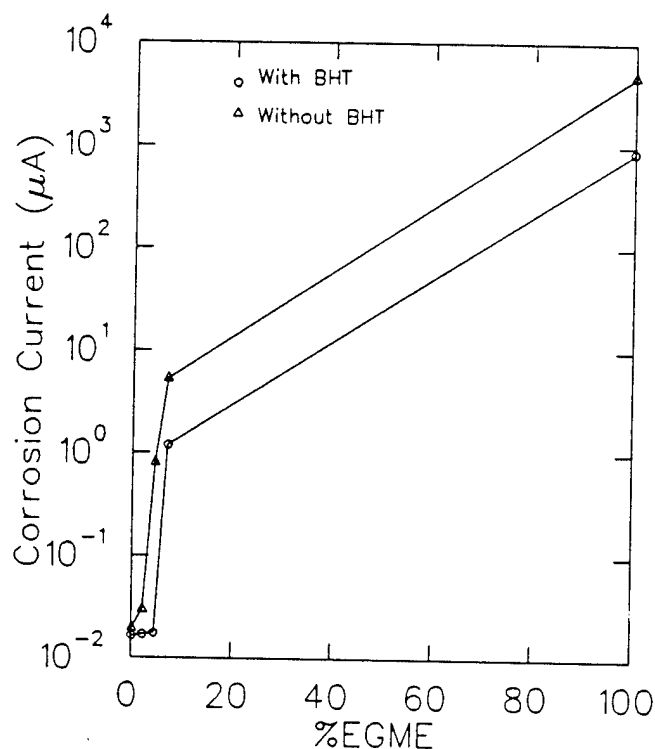
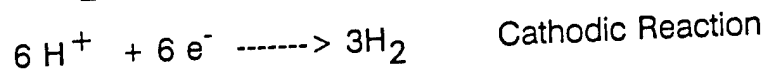
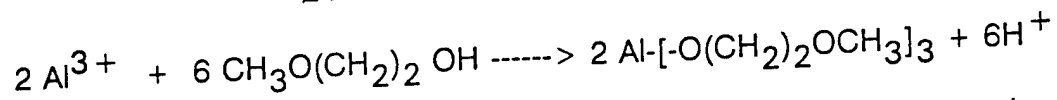
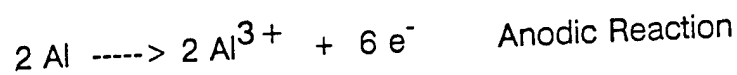


Figure 2

Variation of Corrosion Current Versus Percent EGME in C-10 for AL 2024 (Room Temperature After 22 Days)

The corrosion reactions of Al with EGME/DiEGME could be attributed to the fact that EGME and DiEGME have weak acidic alcoholic hydrogens similar to methanol which react with aluminum forming Al-EGME complex liberating hydrogen ions in the solution. This is consistent with the reaction of methanol with polycrystalline Al in temperatures ranging from 198 K to 500 K reported by Rogers et. al. [13], which indicate the formation of methoxide species on the Al surface

with the formation of hydrogen ions. The reactions suggested are as follows:



hydrogen ions can also react with Al ions making aluminum hydride:

As the concentration of EGME increases the acidic group increases which reacts more vigorously with the Al surface which in turn increases the corrosion current as observed experimentally.

The inhibiting effect of BHT is probably due to a competitive inhibition mechanism. BHT, being a large sterically hindered phenolic compound, adsorbs on the surface of the aluminum forming a film several monolayers thick. The adsorbed BHT molecule competes with EGME for the aluminum surface which eventually decreases the corrosion rate. Phenolic compounds have been shown to inhibit corrosion in dilute salt solutions [14]. This mechanism is evidenced not only in the decreased overall corrosion current, but also by the fact that the corrosion current remains fairly constant until at higher concentrations of FSII the monolayer is broken down.

Visual and microscopic examination of the electrode after 22 days shows that the type of corrosion for EGME was localized pitting corrosion. The number and sizes of pits were found to increase as the concentration of EGME was increased. This type of corrosion is consistent to that found in missiles. The corrosion behavior observed with DiEGME was very similar to that observed with EGME; however, the pit was more diffuse and microscopic examination revealed the presence of intergranular corrosion for an electrode exposed to 4.0 percent DiEGME. No intergranular pitting was found for electrodes exposed to 4.5 percent EGME. Investigations are continuing into this result.

Effect of Temperature on Corrosion Current

The corrosion current as a function of time for Al 2024 in C-10 + 0.1 percent EGME at 0, 8 and 25 °C is shown in Figure 3. For a given temperature, the corrosion current increases as a function of time; however, the corrosion current decreases as a function of temperature.

This decrease as a function of temperature is shown in Figure 4 and is unexpected. Figure 4 indicates that the corrosion rate increases as the temperature is decreased from 25 to 0 °C but starts decreasing as the temperature drops below zero. The results can be explained by the fact that the FSII precipitates out of solution at approximately 0 °C and covers the surface of the Al electrode. Further decrease in temperature does not substantially increase the FSII concentration on the electrode but slows the corrosion rate as normally expected. A separate solubility experiment of EGME in C-10 fuel as a function of temperature was conducted. It was observed that EGME does come out of the solution and adheres as small drops on the walls of the measuring flask. The precipitation of EGME on the electrode in the form of drops increases the concentration at those locations resulting in pit formation.

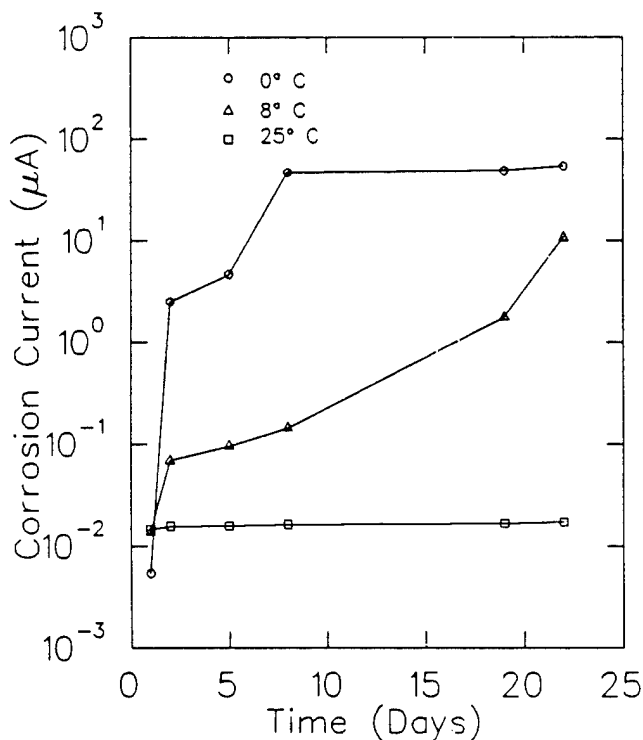


Figure 3
Variation of Corrosion Current With Time at 0, 8, and 25 °C for Al 2024 Exposed to C-10 Plus 0.1 Percent EGME

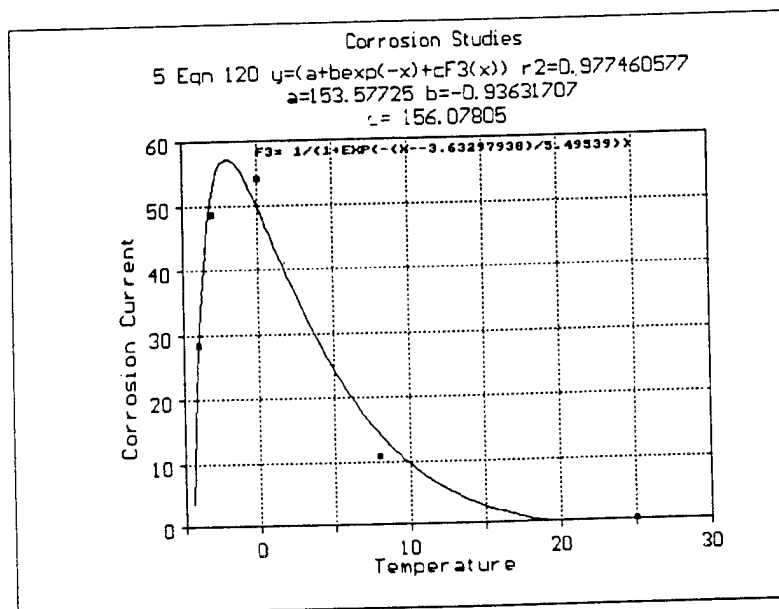


Figure 4
 Variation of Corrosion Current with Temperature for
 Al 2024 Exposed to C-10 Plus 0.1 Percent EGME

Effect of Metals on Corrosion Current

Corrosion current of different alloys in the presence of 0.1 percent and 7.0 percent EGME was determined as a function of time. Figure 5 shows the corrosion current as a function of time in 7 percent EGME for the alloys at 25 °C. The order of corrosion resistance in 7 percent EGME is Al A357 > Al 6061 > Al 2024 > Al 7075. In 0.1 percent EGME the corrosion resistance was reversed for Al 2024 and Al 7075. In all cases the corrosion current was lowest (greatest corrosion resistance) for Al A357.

The results can be explained by taking into account the alloying chemistry. The presence of chromium and silicon as alloying elements has been shown to increase the resistance of Al alloys to corrosion [15]. Al A357 has 7 percent Si and Al 6061 has 0.4 to 0.8 percent Si. These alloys have shown higher corrosion resistance than Al 2024 and Al 7075. The higher corrosion resistance of Al 7075 relative to Al 2024 at lower

FSII concentration is probably due to the presence of 0.18 to 0.28 percent Cr in Al 7075.

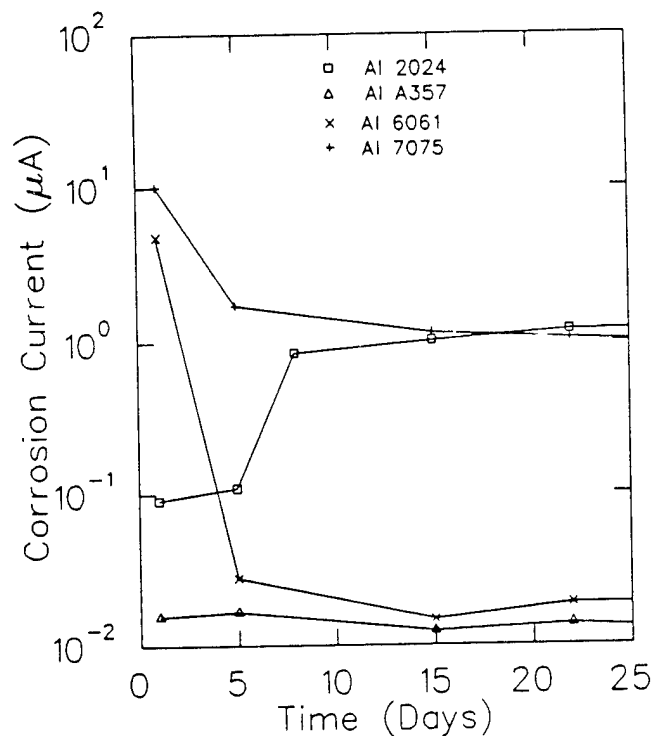


Figure 5
Variation of Corrosion Current with Time for Aluminum Alloys Exposed to C-10 Plus 7 Percent EGME

Effect of Coatings

The corrosion current for Al alloys with different coatings was measured in 0.1 percent and 7 percent EGME to evaluate the coatings' resistance to corrosion. Figure 6 shows the plot of corrosion current as a function time for Al 2024 exposed to C-10 with 7 percent EGME for three coating systems chromic acid anodized, Scotchweld EC 1290® primer coat, and a combination coating of chromic acid anodized and Scotchweld EC 1290® primer coat (topcoat). Initially on day 1, the corrosion current for all coated Al 2024 in 7 percent EGME was higher compared to that of uncoated Al 2024. The corrosion current decreased substantially in 5 days and remained stable for the 50 days of exposure

shown in Figure 6 (these tests are continuing to determine when and if the coating breaks down). Similar results were observed at other concentrations of EGME. These results clearly indicate that anodization and EC 1290 coating protects the Al alloys against corrosion. Additional tests of chemical conversion coating for Al 6061 have also shown similar corrosion resistance in 0.1 percent and 7 percent EGME solutions. Other testing is being conducted, on the coating systems, at lower temperatures to examine the effect of temperature on corrosion resistance.

That the corrosion current for coated samples are orders of magnitude higher initially but drop down considerably in 5 days is not fully understood at this time. However, it is known that the surface contamination by trace metals such as Cr, Zn, etc., (which is normally used during anodization and in primers) could contribute to higher corrosion current. It is postulated that contaminants are leached from the surface initially and reacted. This process cleans the surface and further corrosion reactions are inhibited by the coating system.

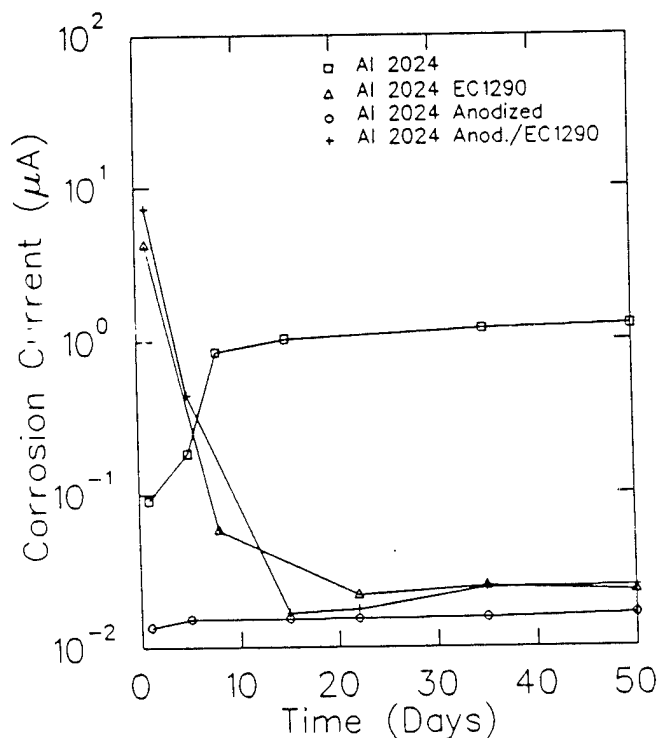


Figure 6
Variation of Corrosion Current with Time for Coated and Uncoated AL 2024 in C-10 Plus 7 Percent EGME

SUMMARY

An accelerated test method using AC Electrochemical Impedance Spectroscopy has been developed and used to measure the corrosion current in JP-10 missile fuel, a low conductivity, nonpolar solution. There is a general agreement in the trend between the experimentally observed values of corrosion current and corrosion resistance behavior of alloys. The corrosion current increases as a function of FSII concentration confirming the hypothesis that it is this additive that is responsible for the corrosion of aluminum fuel system components. Addition of BHT in a mixture of C-10 and EGME inhibits the corrosion of Al alloys. A decrease in temperature results in an increase in the corrosion current, due to the precipitation of FSII onto the aluminum surface, until a maximum corrosion current is reached between 0 and -3 °C. Of the four alloys tested Al A357 shows the highest corrosion resistance due to the presence of Si as an alloying element. Lower corrosion resistance was observed for Al 2024 and Al 7075 due to the absence of Si or Cr. Results to date of experiments involving anodization, Scotchweld EC 1290® epoxy primer, and chem film coating systems indicate that these coatings protect the aluminum surface against corrosion. It is clear from these results that EIS can be used as a technique to detect very small amounts of corrosion in low conductivity media and be used to evaluate solution chemistry, alloy corrosion resistance, and protective coatings.

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